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<p>(54) Title: ARYLLITHIUM PROCESS</p> <p>(57) Abstract</p> <p>A process for producing high purity stable etherical solutions of aryllithium compounds by reacting lithium metal, in the form of a dispersion, with a monohaloaryl compound in an ether of the formula ROR' wherein R and R' are independently selected from alkyl radicals containing three to eight carbon atoms, the mole ratio of ether to monohaloaryl compound is at least 1.0 and the reaction temperature is maintained below 65 °C.</p>			

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ARYLLITHIUM PROCESS

This invention concerns a process for producing aryllithium compounds and certain novel aryllithium compositions.

The preparation of aryllithium compounds by the direct reaction of an organic halide with lithium metal in an ethereal solvent has long been known. Ethereal solvents are employed due to the insolubility of aryllithium compounds in hydrocarbon solvents. It is well known that aryllithium compounds react with ethers, resulting in cleavage of the ether linkage and destruction of the aryllithium compound [Gilman, Haubein and Hartzfield, J. Org. Chem. **19**, 1034 (1954); Gilman and Gaj, J. Org. Chem. **22**, 1167 (1954); Barwell, R.L. Chem. Revs., **54**, 615 (1954)]. Ether cleavage is reduced or stopped by preparing and/or storing the aryllithium solutions at low temperatures of -35° to -60°C.

U.S. Patent 3,197,516 advises that "Solutions of aryllithium compounds, such as diethyl ether solutions of phenyllithium, are not stable under conditions of ordinary storage due to the reaction of phenyllithium with ether." This U.S. Patent overcomes these problems of lack of hydrocarbon solubility and stability in ether solutions by using mixed ether/hydrocarbon solvent reaction mediums that contain at least enough ether to solubilize the aryllithium. A slightly different solution to this process problem is disclosed in U.S. Patent 3,446,860 which discloses reacting an ether solution of an arylhalide with a hydrocarbon dispersion of lithium metal to produce stable ether/hydrocarbon solutions of aryllithium compounds.

While these mixed ether/hydrocarbon solutions of aryllithium compounds are useful and produced and sold

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in commercial quantities, highly stable solutions of aryllithium compounds are very desirable for many uses.

The present invention provides a process for producing high purity, thermally stable ether solutions of aryllithium compounds by reacting a dispersion of lithium metal with a monohaloaryl compound in an ether of the formula ROR^1 wherein R and R^1 are independently selected from alkyl radicals containing three to five carbon atoms. R and R^1 may be the same or different alkyl radicals. The ratio of ether to monohaloaryl compound is at least 1.5 to 1, and the reaction temperature is maintained between 5°C and 65°C, preferably 15°C to 40°C and most preferably in the range of about 30°C to 35°C. The preferred mole ratio of ether to monohaloaryl compound is 1.7-2.0 to 1. For example, when using di-n-propyl ether, di-n-butyl ether or di-n-pentyl ether and monochlorobenzene the preferred mole ratio of ether to aryl compound is at least 1.5 and the most preferred ratio is about 1.7. Very high ratios of ether to monohaloaryl compound, such as 6 to 1 or higher, can be used but the product can thereby become rather diluted.

Ethers used in the practice of this invention are of the formula ROR^1 wherein R and R^1 are generally independently selected from alkyl groups containing at least 3 carbon atoms; R and R^1 can be the same or they can be different. Mixtures of ethers can, of course, be employed. Typical ethers useful in practicing this invention include, but are not limited to di-n-butyl ether, di-n-pentyl ether, di-n-propyl ether, and the like. Preferred ethers include di-n-butyl ether, di-n-pentyl ether and di-n-propyl ether.

It is an advantage of the present invention to provide a process which produces aryllithium compounds of high purity and in a high yield process that can be

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conducted at temperatures up to about 65°C, preferably at temperatures of 15° to 40°C. Higher reaction temperatures can be employed with the higher carbon content ethers. When di-n-hexyl ether was employed the 5 reaction at 35-40°C was extremely slow compared to ethers with a lower carbon content. Lower temperatures of 0° to -60°C as disclosed by Gilman, et al., can be employed, but such low temperatures are not desirable due to the cooling costs and low rate of reaction.

10 The process is conducted in an inert atmosphere to protect the aryllithium products which are degraded by contact with a reactive atmosphere such as air containing any appreciable amounts of water vapor. The inert atmosphere is typically a noble gas and preferably 15 argon or helium.

15 The reactants are employed in about stoichiometric amounts with a slight excess of lithium dispersion being preferred to ensure the reaction proceeds to completion; the excess lithium is easily removed and 20 recovered by conventional means. The desired final aryllithium concentration is dependent on the amounts of reactants used. The concentration of the aryl-lithium compounds in the recovered solutions will range in general from about 1 up to about 35 weight percent 25 depending on the solubility of each aryllithium compound. Solutions of 5 to 24 weight percent are preferred. Higher concentrations are possible but they may not be stable at low temperatures often encountered in shipping products in cold climates.

30 Surprisingly, compositions containing 5 to 14 weight percent phenyllithium dissolved in di-n-butyl ether are not pyrophoric. Concentrations of about 14 weight percent and less are not pyrophoric, while concentrations of 24 weight percent and above are 35 pyrophoric.

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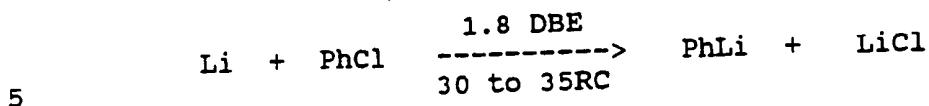
While, in the most preferred embodiment of the present invention the aryllithium compound is phenyllithium, various other aryllithium compounds, for instance biphenyllithiums, such as 2 biphenyllithium, 5 3-biphenyllithium and 4-biphenyllithium; alpha-naphthyllithium; are definitely contemplated and encompassed by this invention.

Therefore included, by way of further example, are the group of aryllithium compounds which result from 10 the utilization, in the practice of the methods disclosed herein, of monohaloaryl compounds such as monohalobenzenes, exemplified by chlorobenzene and bromobenzene; monohaloalkylbenzene compounds, exemplified by o,m,p-bromotoluene, and p-bromoisobutylbenzene, and polynuclear haloaryl compounds exemplified by α -bromonaphthalene, 4-bromobiphenyl, and 9-bromoanthracene. Other haloaryl compounds with 15 functional groups which can be used are alkoxyaryl halides exemplified by o-anisylbromide, 3-isobutoxy-4-bromotoluene, and 2-chloro-3-methyl-4-ethoxytoluene; dialkylaminoarylhalides exemplified by p-bromodimethylaniline, and 2-bromo-3,4-dimethyl-N,N-diethylaniline; heterocyclic aryl halides, exemplified by 4-bromo-10-ethyl-phenothiazine; o-bromodiphenylsulfone, and 4-bromobenzothiophene; and aryl halides 20 containing other metallic or metalloidal groups, exemplified by p-bromophenyl di-n-propylarsine, and p-bromophenyl trimethylsilane.

Aryllithium compounds, for example, phenyllithium, 30 are synthesized in a single-pot via the reaction of monochlorobenzene with lithium dispersion in di-n-butyl ether (DBE) as shown by the following chemical equation:

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Equation 1



10 In order to control the exothermic reaction, the
chlorobenzene is added dropwise to the stirred lithium
slurry in DBE. After reaction and a minimum of two
hour post-reaction time (preferably overnight), the
reaction mass is filtered to remove lithium chloride
and excess lithium metal. A light amber colored solu-
tion of phenyllithium (~25 wt. %) in DBE is obtained.

15 The phenyllithium is stable at room temperature (20-22°C) and at elevated temperature (40°C) for at least 40 and 30 days, respectively. The final product is assayed by total alkalinity titration, Watson Eastham titration for active carbon-bound lithium, GLC 20 for purity and by NMR analysis to determine the mole ratio of ether to phenyllithium.

The following examples further illustrate the invention. In the examples all proportions are by weight, all temperatures are in degrees Celcius ($^{\circ}\text{C}$), and pressures are atmospheric, unless indicated otherwise.

Exemplary Run (361-72)

30 The following materials and equipment were
employed: 27.8 g lithium dispersion, 30 wt.% in mineral
oil containing 0.75 wt.% Na (based on lithium content)
lithium = 1.2 moles; 58.6 g monochlorobenzene (0.52
moles); 117.2 g di-n-butyl ether (0.90 moles); 10 ml
35 phenyllithium in di-n-butyl ether (DBE) (0.021 Moles)
used as lithium metal conditioner, and the following
laboratory equipment: round bottom, 3 neck reaction

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flask (500 ml.) with a gas inlet; thermometer, filter funnel, fine porosity (500 ml); mechanical stirrer with associated equipment; and cooling bath (dry-ice/hexane).

5 All glassware was baked in an oven (~150°C) for several hours, then assembled and purged with argon until cool. To protect the final product an argon atmosphere was maintained throughout the reaction, the filtration, and packaging. Lithium dispersion (1.2 moles) was washed in the filter funnel with aliquots of hexane followed by DBE (100 ml each) and then transferred to the reaction flask along with di-n-butyl ether (117.2 g). Next 10 ml phenyllithium solution was added to the slurry which was then stirred for ~1 hour in order to condition (activate) the lithium. The metal/organic halide reaction was then initiated by the addition of 2 ml of monochlorobenzene. The initiation was rapid as evidenced by a 6 degree rise in temperature. The remaining organic halide was added dropwise over the next 42 minutes while controlling the reaction temperature between 30 and 35°C. The reaction mass gradually cooled to ambient during the next hour indicating some post reaction was occurring. The reaction mass was slowly stirred overnight to ensure complete reaction of the chlorobenzene.

20 Filtration of the final product to remove by-product lithium chloride and residual lithium metal was very rapid (~5 minutes). The filter cake was stirred with an additional 50 ml of DBE which was also filtered. The DBE/filter cake wash was combined with the main filtrate to yield 182 g of a clear light amber solution of phenyllithium in DBE.

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Analytical Results:

	Total Base	= 2.32 M (24.1 wt. %)
	W.E. Titration	= 2.28 M
	NMR	= 2.34 M (24.2 wt. %)
5		= 2.0 mole ratio DBE/PhLi
	GLC	= 0% residual monochlorobenzene
	Density	= 0.81 g/cc
	Yield	= 96.1 %

10 The procedure of this Exemplary run 361-72 was repeated a number of times in further experiments discussed herein; the experimental details are reported in the tables.

15 Phenyllithium was synthesized in this new process via the reaction of monochlorobenzene and lithium dispersion in a high boiling ether, di-n-butyl ether (DBE - see Equation 1). Equation 1 shows the use of 1.8 equivalents of DBE/chlorobenzene which resulted in extremely high yields of phenyllithium (see Table III, 20 Exp. No. 6778 - yield = 93.4%, and Exp. No. 361-72 - yield = 96.1%). Filtration of these light amber colored solutions of phenyllithium was very rapid.

25 The use of less ether (DBE/chlorobenzene = 0.9 mole ratio) in an attempt to produce a more concentrated phenyllithium solution (~35 wt. %) resulted in a lower yield (50.6%) indicating that more DBE was needed to obtain high yields (see Table III, Exp. No. 361-68). Two other duplicate experiments utilizing a mole ratio of DBE/chlorobenzene = 1 and cyclohexane as co-solvent 30 resulted in slow initiation, sluggish reaction and essentially no yield (see Table III, Exp. No. 6776 and 6777).

35 Thus, to achieve high yields and sufficient concentration of phenyllithium (25 wt. %) a mole ratio of at least 1.8 DBE/chlorobenzene is required. The

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reaction should be carried out in pure DBE containing no hydrocarbon co-solvent. Also, to avoid deactivation of the lithium the reaction should be conducted on the same day that the lithium and DBE are brought into contact. Because less fine lithium chloride is produced in the new process due to fewer side-reactions, filtration of the final product was extremely fast.

Due to fewer side-reactions phenyllithium synthesized in DBE was of very high purity. Samples of phenyllithium in DBE (see Table II, Exp. No. 6878) and a commercially available phenyllithium in ethyl ether/cyclohexane (FMC Corporation, Lithium Chemical Division Plant) were analyzed by gas liquid chromatography (GLC also termed GC) employing "active" and "hydrolyzed" injection techniques. This method differentiates between lithium bearing and non-lithium bearing species. First, an active (non-hydrolyzed) sample of phenyllithium was injected into the cool (50°C) injection port of the GLC and the volatile compounds measured were essentially zero. This GC scan was compared to a GC scan of a hydrolyzed sample of phenyllithium run under the same GC conditions to determine which compounds were non-volatile or lithium bearing species. Hydrolysis converts phenyllithium into benzene and lithium hydroxide. The results of the comparison study are shown in the following Table I.

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TABLE I
GLC COMPARISON PHENYLLITHIUM
SYNTHESIZED IN DBE AND IN ET_2O /CYCLOHEXANE

Compounds Detected	DBE	Diethyl ether/ Cyclohexane
Phenyllithium (% purity)	>99	>95
Biphenyl (mole %)	0.63	0
Lithiated Biphenyl (mole %)	0	5.5
Chlorobenzene (mole %)	0(a)	0(b)
Free benzene (GLC %)	0.5	(c)
Color of solutions	light amber	black

- a. Phenyllithium freshly prepared
- b. Aged phenyllithium (7 mos)
- c. Under these GC conditions benzene could not be separated from cyclohexane.

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The above Table shows that the new process produced high purity phenyllithium which contained only a small amount of non-lithiated biphenyl (0.63 mole % based on contained PhLi). On the other hand, the commercially 5 available phenyllithium in diethyl ether/cyclohexane solvent contained a significant amount of lithiated biphenyl and/or the lithium adduct of biphenyl (5.5 mole %) either of which, as organometallics, would enter into subsequent synthesis reactions along with 10 phenyllithium. These lithium bearing impurities compete with desired aryllithium compounds in reactions and form unwanted products.

These impurities are present because of side 15 reactions which occur during and after the organic halide/metal reaction. The side reactions include the following:

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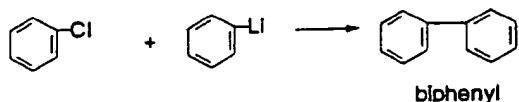
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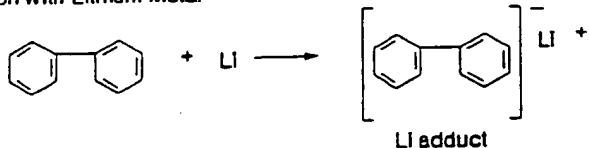
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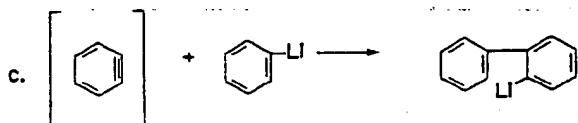
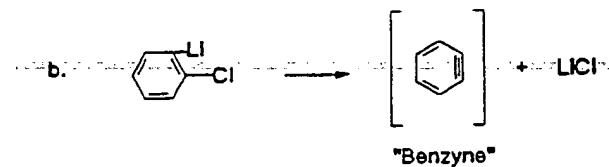
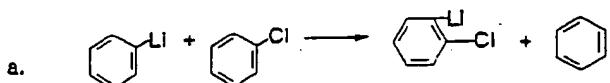
1. Wurtz coupling



2. Adduction with Lithium Metal



3. Metalation of chlorobenzene to form a "Benzyne" Intermediate



This coupling reaction, which not only generates both biphenyl and extremely fine lithium chloride, can be controlled by temperature of reaction, halide feed rate and use of excess lithium. Also, coupling can be affected by the polarity of the ether employed as solvent. For example, the synthesis of phenyllithium in limited THF/cyclohexane (THF/PhCl = 0.96 mole ratio) resulted in a low yield (43.9%) when all the THF was in the reaction flask at the beginning of reaction (see Table III, Exp. No. 6694). In a duplicate experiment coupling was controlled by placing 80% of the THF in

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the addition funnel along with the chlorobenzene to achieve a high yield (96.4%). However, the product precipitated from solution as the 1:1 phenyllithium/etherate (see Table III, Exp. No 6702). In ethyl ether 5 employing no co-solvent a low yield of phenyllithium (72%) was recorded (see Table III, Exp. No 4196). In pure THF Gilman(4) reported that low temperatures (-60°C) controlled coupling and obtained high yields (92%). At higher temperatures yields were 10 progressively worse (e.g., yield = 77% at -35°C). Now, it has been discovered that phenyllithium can be synthesized in high yield in a totally ether solvent (DBE). In the less labile ether (DBE), Wurtz coupling was essentially inhibited as evidenced by the fact that 15 only a trace of biphenyl (0.63 mole % based on PhLi content) was found in the new phenyllithium (see Table I above).

Adduction with lithium metal can generate a biphenyl lithium adduct. In more labile ethers such as 20 THF and ethyl ether adduction readily occurs causing the characteristic black coloration of phenyllithium. Adduction does not occur in the synthesis of phenyllithium in DBE as no lithiated aromatic species was found in the final product (see Table I, above).

25 Metalation of chlorobenzene to form a "benzyne" intermediate may occur. The formation of lithiated biphenyl may occur during reaction or after filtration if residual (unreacted) chlorobenzene is in the final solution. This side-reaction is slow and can be 30 controlled by employing excess lithium metal (10 to 20%) to ensure complete reaction and sufficient post-reaction time. In DBE, this side-reaction was avoided because no lithiated biphenyl or residual chlorobenzene was found in the final filtered product (see Table I, 35 above).

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To show that side-reaction does occur 0.1 equivalents of chlorobenzene was added to 50 ml phenyllithium solution (Exp. 6778 - 2.38M.). After 36 hours no precipitation of lithium chloride was noted 5 indicating this reaction to be slow in DBE. However, during the course of 8 days a white precipitate (LiCl) appeared on the walls of the bottle. GLC analysis using the previously described "active" and "hydrolyzed" injection techniques indicated the phenyl-10 lithium to contain a near quantitative amount of lithiated biphenyl.

In summary, high yields of phenyllithium can be synthesized in DBE because the known side-reactions are virtually eliminated. The final product was extremely 15 pure containing no lithiated impurities or residual chlorobenzene.

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TABLE II
THERMAL STABILITY OF PHENYLLITHIUM
IN DBE (EXP. NO. 6778)

Date	Number Days	Temp. °C	Total Base M.	Active(1) C-Li M.	DBE/PHLi(2) mole ratio
1/15/90	0	start	2.38	2.35	1.90
Remarks: Solution Clear/Light Amber					
1/22/90	7	40(3)	2.38	2.42	1.86
Remarks: No change in appearance					
1/29/90	14	40(3)	2.40	2.32	1.88
Remarks: Solution Light Amber; Slight Amount of Solids					
2/5/90	21	40(3)	2.39	2.36	1.82
Remarks: Solution Light Amber; Slight Amount of Solids					
2/12/90	30	40(3)	2.38	2.42	1.82
Remarks: Solution Light Amber; Slight Amount of Solids					
2/22/90	40	RT(4)	2.39	2.36	1.86
Remarks: Solution Clear, Light Amber, Slight Amount of Solids					

1. Determined by W.E. titration: Watson, S.C. and Eastman, J.F., J. Organomet. Chem. 9, 165, (1967).
2. Determined by NMR analysis.
3. Sample bottles of phenyllithium were placed in a constant temperature bath ($40 \pm 0.5^\circ\text{C}$) for the tests.
4. RT = room temperature. ($20-21^\circ\text{C}$)

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As Table II shows phenyllithium in DBE (24.7 wt.%) was found to be stable at an elevated temperature (40°C) and at room temperature (20-21°C) for 30 days and 40 days, respectively. This was shown by total base and active carbon-lithium analyses and, also, confirmed by NMR which quantitatively measured phenyllithium and di-n-butyl ether during the testing period which demonstrated that there was no cleavage of the ether or degradation of the phenyllithium. For the first time phenyllithium has been shown to be stable in a totally ether solvent.

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TABLE III
SYNTHESIS OF PHENYL LITHIUM IN VARIOUS SOLVENTS

Exp. No.	REAGENTS				ANALYTICAL RESULTS				Yield %	Remarks
	Li ¹ Moles	PhCl ² Moles	Lewis Base Type	Co-Solvent Moles	Total ml.	W.E. Base H.	Titre. ³ H.	Ether/ PhLi ⁴ Mole Ratio		
6694 ^B	2.05	0.52	THF	0.50	Cyclohex	160	0.81	2.24	43.9	All THF in Rx flask.
6702 ^B	1.51	0.50	THF ⁵	0.50	Cyclohex	160	1.00	96.4	80% THF in addn. funnel.	
6719 ^B	1.20	0.50	THF	0.49	Cumene	160				No Reaction.
4196 ^B	1.10	0.50	Et ₂ O ⁶	2.70	None		0.90	8.80	72.0	All ether in Rx flask.
6776	1.20	0.50	DBE ⁷	0.50	Cyclohex	75				No Reaction.
6777	1.46	0.50	DBE	0.50	Cyclohex	75				No Reaction.
6778	2.81	1.04	DBE	1.76	None		2.38	2.35	1.90	93.4
361- 72	1.20	0.52	DBE	0.90	None		2.32	2.28	2.00	96.1
361- 68	1.20	0.50	DBE	0.45	None		2.51			50.6
										All DBE in Rx flask.

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TABLE III - Continued
SYNTHESIS OF PHENYL-LITHIUM IN VARIOUS SOLVENTS

Expt. No.	REAGENTS						ANALYTICAL RESULTS					Remarks
	Li ¹ Moles	PhCl ² Moles	Lewis Base Type	Co-Solvent Type	W.E. ml.	Total Base M.	W.E. Titra. M.	Ether/ PhLi ⁴ Mole Ratio	Yield/ %			
361- 93	1.44	0.60	DBE ⁶	3.60	None	1.25	4.35	91.1			Dilute run employing more DBE.	
7092	0.60	0.25	DPE ⁹	0.97	None	1.67	1.64	4.10	94.6		All DPE in Rx flask.	
7265	1.1	0.28	DAE ¹⁰	0.50	None	2.08	-	1.8	91.0		All DAE in Rx flask.	

1 Employed lithium dispersion containing 0.5 to 0.75 wt. % sodium

2 PhCl - monochlorobenzene

3 Active carbon-bound lithium analysis; Watson S.C. and Eastman J.F. J. Organomet Chem., 9, 165, (1976)

4 Determined by NMR

5 THF - tetrahydrofuran

6 Et₂O - ethyl ether

7 DBE - di-n-butyl ether

8 Comparison example

9 DPE - di-n-propyl ether

10 DAE - di-n-pentyl ether

Rx flask = reaction flask

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Claims:

1. A process for producing high purity thermally stable solutions of aryllithium compounds by reacting lithium metal with a monohaloaryl compound in an etheral solvent characterized by reacting a dispersion of lithium metal with a monohaloaryl compound in an ether of the formula ROR' wherein R and R' are independently selected from alkyl radicals containing three to eight carbon atoms and the mole ratio of ether to monohaloaryl compound of at least 1.5 and the reaction temperature is maintained between 5°C and 65°C, with the proviso that the ether contains at least six carbon atoms.
2. The process of claim 1 characterized in that the monohaloaryl compound is selected from monochlorobenzene, monohalobiphenylbenzene, monohalonaphthalene, monohalophenanthrene, ortho-halotoluene, meta-halotoluene and para-halotoluene.
3. The process of claim 1 or 2 characterized in that the monohaloaryl compound is selected from monochlorobenzene and monobromobenzene.
4. The process of claim 1 or 2 characterized in that the halo radical is selected from bromo and chloro.
5. The process of claim 1 characterized in that the ratio of ether to monohaloaryl compound is in the range of 1.5-2.0 to 1.
6. The process of claim 4 characterized in that the ratio of ether to monohaloaryl compound is 1.7 to 1.
7. The process of claim 1 characterized in that the temperature is maintained between 30° and 35°C.
8. A process for producing high purity phenyl-lithium by reacting lithium metal with a mono-halobenzene in a liquid ether characterized by reacting

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a dispersion of lithium metal with a monohalobenzene selected from monochlorobenzene and monobromobenzene, the ether is selected from di-n-butyl ether, di-n-pentyl ether and di-n-propyl ether and there is a mole 5 ratio of ether to monohalobenzene of at least 1.5 and the reaction temperature is maintained below 65°C.

9. The process of claim 8 characterized in that the ether is di-n-butyl ether and the ratio of ether to monohalobenzene is in the range of 1.5-2.0 to 1.

10. The process of claim 8 characterized in that the ratio of di-n-butyl ether to monohalobenzene is 1.7 to 1.

11. The process of claim 8 characterized in that the temperature is maintained between 30° and 35°C.

15. The process of claim 1 or 8 characterized in that the ether is di-n-propyl ether.

13. The process of claim 1 or 8 characterized in that the ether is di-n-pentyl ether.

20. The process of claim 1 or 6 characterized in that the monohaloaryl compound is selected from the group consisting of monochlorobenzene and monobromobenzene.

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US92/01208

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :C07F 1/02, C07F 1/04, C07F 1/06, C07F 3/02, C07F 3/04
 US CL :260/665.R

According to International-Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 260/665.R

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CAS/APS/BEILSTEIN

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 3,197,516 (ESMAY ET AL.) 27 July 1965, See entire document.	1-14
Y	US, A, 3,446,860 (BEUMEL) 27 May 1969, See entire document.	1-14
Y	Electrochim. ACTA. vol. 34, no. 11, pg. 1529-1534 (1989) Holding et al., A Chemical Approach to the Study of the Films on Lithium in Organic Electrolytes for Batteries.	1-14

 Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:	
A document defining the general state of the art which is not considered to be part of particular relevance	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

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